



(19) Japan Patent Office (JP) (12) Laid-Open Patent Gazette (A) (11) Japanese Unexamined Patent
06-256067

(43) Date of publication: 9/13/94

(51) Int. Cl.⁵ Domestic classification Patent Office File No. Technical Indications
CO4B 37/00 A FI

Request for examination: Not yet made. Number of claims: 4 FD (Total of 7 pages)

(21) Filing number: 05-065909

(22) Application date: 3/3/93

(71) Applicant: Toshiba Ceramics Co. Ltd.
1-26-2 Nishi-Shinjuku, Shinjuku Ward, Tokyo

(72) Inventor: Masaru Shimpo

(74) Agent: Makiko Akano, Patent Attorney (plus two others)

(54) Title of the invention: Compound for joining ceramics

(57) Abstract:

OBJECT: To provide a compound for joining ceramics, capable of strongly joining the various ceramics in a simple process, and capable of forming joined layers and joined products having sufficient joint strengths in processes before firing and during firing processes and possessing superior properties such as high purity, heat resistance, and high chemical resistance.

CONSTITUTION: A ceramics joining compound formed by kneading a polysilazane compound and a polycarbosilazane compound—known as the precursors of silicon carbide (SiC) and silicon nitride (SiN)—with ceramic powder and a solvent is used as a joining material for ceramics.

Claims

1. A ceramics joining compound comprising a polysilazane compound, a polycarbosilazane compound, ceramic powder and a solvent.
2. A ceramics joining compound according to claim 1, in which said ceramic powder is of the same type as the ceramics to be joined or has a similar coefficient of thermal expansion.
3. A ceramics joining compound according to claims 1 or 2, in which the weight ratio of said polysilazane compound and said polycarbosilazane compound is 1:0.05-40.
4. A ceramics joining compound according to claims 1, 2 or 3, in which the weight ratio of said ceramic powder and the sum of said polysilazane compound and said polycarbosilazane compound is 1:2-40.

Detailed Description of the Invention

1. Industrial Field of Use

The present invention relates to a compound that is suitable for joining and filling in gaps in an extensive variety and range of ceramics, such as non-oxide ceramics like silicon, silicon carbide, silicon nitride, aluminum nitride and compounds made up of combinations of these, and oxide ceramics like alumina, zirconia and mullite.

2. Prior Art

Ceramics have many merits, such as being highly heat resistant and strong, chemically inert and capable of extremely pure preparation, and are an advanced material used in a variety of ways. Processing of ceramics is usually done at the ceramic forming stage on unfired materials. However, as there is a big volume change in the ceramic form before and after firing, it is difficult to increase dimensional accuracy with only pre-firing processing. Therefore, while it is possible to reprocess in order to obtain the desired shape and accuracy after firing, there is a limit to the shapes and sizes possible, as ceramics are hard, fragile and have poor workability, as mentioned above.

3.

Conventionally, by assembling and joining each separate part to form the desired ceramic form, complex forms and large parts have been formed. In this case, if each of the ceramic fired parts cannot be joined in the prescribed form while maintaining heat-resistance and chemical durability, which are the points of superiority of ceramics, the intrinsic usage value of ceramics is compromised. Therefore, as a means of joining ceramics, a variety of methods that have heat resistance are being implemented. For example, there are methods such as joints that use

soldered glass or metalizing joining methods. Another example is where some cement-type bioinorganic materials such as alumina cement are used.

4. Problems this Invention Seeks to Solve

However, both the abovementioned soldered glass join and metal join methods could only be applied to limited materials, and there was insufficient heat and corrosion resistance. Moreover, a high level of technology is required to make the join and the join part is limited to simple things. Further, while inorganic joining materials have the advantage of adhering at room temperature, they usually need to be fired at temperatures of 1000°C or above to become fire resistant, and during the firing process, the adhesive power decreases remarkably and cracks occur, which causes much damage, so they can only be used for an extremely limited amount of materials and purposes. Many inorganic joining materials also contain a wide variety of element ingredients in the form of components or impurities. It is not possible to achieve the prescribed level of high purity.

5.

The present invention has taken the above situation of ceramics joining methods into account and aims to provide a ceramic joining material, namely a ceramic joining compound that enables firm joining of all types of ceramics with a simple process, and that has sufficient joining strength on pre-fired materials and during the firing process and that can form joining layers and joins superior in high purity, high heat resistance and high chemical resistance; and yet another aim is to easily form integrated ceramics of complex shapes and large objects through the firmly fixed joins.

6.

As a result of study directed toward all types of requirements of a joining material that achieves the abovementioned aims, and as a result of diligent study to satisfy the following two points in particular, the present inventor arrived at the present invention. That is:

(1) The joining material can express sufficiently strong fixing strength at room temperature when being joined, and the joining material maintains fixing strength even during the firing process. That is, there are no concerns about the joined part separating during the firing process and no special firing jig is required. Moreover, no limitations are placed on the shape or size of the joined body, and, further, should circumstances permit, by making the ceramic joined body usage temperature in the range of firing temperatures, the firing process after joining can be omitted.

(2) As a high level of purity is required for ceramic joining materials, contaminants such as transition metals or alkali metal ions for example, shall not be included as an ingredient or an impurity. Ceramics are very often used as materials for purposes where a high degree of purity is required such as the manufacture of electronic parts or semiconductor elements, and in these uses, it is necessary to prevent the abovementioned contaminants commingling, from the raw materials to during the ceramics manufacturing process or processing. Therefore, when the joined ceramic joined form will be used particularly for semiconductor element processing, all

elements are contaminants and shall be reduced as much as possible, except for elements such as Si, O, N, C, and H.

7. Means for Solving these Problems

The present invention is a ceramic joining compound which comprises a polysilazane compound, a polycarbosilazane compound, a ceramic powder and a solvent.

8. Actions for Solving these Problems

The present invention comprises the abovementioned, wherein polysilazane and polycarbosilazane compounds are dissolved in a prescribed solvent to form an adhesive liquid, and that liquid is applied to the join part of the ceramic to be joined and by drying it, ceramics are easily fixed in place and joined, and subsequently maintain fixing strength even during firing. Further, if heat is applied to the polysilazane and polycarbosilazane compounds under an inert gas or oxygen-containing gas atmosphere, that atmosphere generates heat-resistant, chemically stable compounds such as SiN, SiC, SiON, Si, and SiO, and forms a strong joining layer with the mixed ceramic powder, and a strong joined body of ceramics can be obtained. Moreover, polysilazane and polycarbosilazane compounds can be chemically synthesized and it is easy to achieve a high level of purity, whereby they are not a source of contamination and are a joining material for all types of ceramics such as semiconductor parts, as they do not include impure elements that can harm semiconductors and the like.

9.

The present invention is explained in detail below. The polysilazane and polycarbosilazane compounds used in the present invention are widely known as the precursors of silicon carbide (SiC) and silicon nitride (SiN). Polysilazanes can use compounds such as the perhydropolysilazane polymer at various molecular weights and all types of methylpolysilazane polymers, which are conventionally used as precursors of SiN and SiC. Polycarbosilazanes are generally expressed as $RR \sim SiCH_2 \sim$ (however, R and R' are $R=R'$, and any of H, CH₃, C₃H₅, and n=5-5000 and above), and can use compounds that have been conventionally used as SiC precursors.

Comment: I could not read the letters on any of the PDFs. Parts that I could not read are marked with "~". Is it any clearer on the version you have?

10.

According to the knowledge of the present inventor, both the abovementioned polysilazane and polycarbosilazane compounds after being dissolved in an organic solvent such as xylene produce fixing strength at room temperature levels when the solvent has been eliminated, but the fixing strength changes with temperature increases. That is, the inventor conducted an experiment to investigate the relation between temperature and fixing strength on a polysilazane compound, a polycarbosilazane compound and a compound of the two at a ratio of approximately 1:1. The results are shown as a graph in Diagram 1.

As Diagram 1 shows, the fixing strength of a polysilazane compound, that is, the binding strength, shows a tendency to virtually disappear at 100-200°C, but rapidly increase from the 200°C mark while then decreasing its rate of increase at the 500°C mark, and once again rising higher at 900-1000°C. Polysilazane compounds range from solid to viscous liquids when in the neighborhood of room temperatures, depending on the type of compound or degree of polymerization, and when the temperature increases, along with a low viscosity liquid being generated, a decomposition reaction occurs and an exceedingly fragile gel is generated, which reduces the adhesive strength. At 200°C and above, as polymerization continues and the gel solidifies, the adhesive strength increases but in the neighborhood of 500°C, thermal cracking is pronounced and organic substances disengage in large amounts, leaving a porous residue, which slows the increase in fixing strength. Further, at approximately 900-1000°C thermal cracking ceases and crystallization and sintering of the inorganic compound generated continues, and the inference is that the adhesive strength continues to rise even more dramatically.

11.

In the case of the polycarbosilazane compound, as shown in Diagram 1, at approximately 200-400°C, fixing strength disappears, but at around 400°C and above, fixing strength increases along with the temperature increases, while the rate of strength increase diminishes when it exceeds 600°C, and in the same way as the polysilazane compound, at 900-1000°C, it shows a tendency to once again increase further.

Most polycarbosilazane compounds are solid in the neighborhood of room temperatures and usually maintain stability and fixing strength up to the 200°C range. However, when temperatures rise above 200°C, these compounds become low viscosity liquids, a polymerization reaction occurs, and binding strength is lost for the first time. However, at 400°C and above, fixing strength increases along with temperature as high polymerization occurs. Usually, polycarbosilazane compounds are much stronger than polysilazane since a gelation reaction does not occur. At temperatures above 600°C, as is the case with polysilazane, thermal cracking of solidified parts progresses and the compound becomes porous, which lowers the rate of strength increase but at approximately 900-1000°C and above, thermal cracking ceases and binding strength again increases dramatically along with temperature increases.

12.

As is clear from Diagram 1, when a polysilazane compound and a polycarbosilazane compound are used alone, temperature ranges where fixing strength is virtually lost appear for both compounds as temperatures rise. When the two are combined and used together, as in the present invention, it is understood that at almost all temperature ranges, a binding strength that exceeds the average rate of both separate compounds can be achieved. The reasons for this are not clear, but in the neighborhood of 100-200°C where polysilazane fixing strength disappears, since polycarbosilazane is a solid or a highly viscous liquid, gelation of polysilazane is thwarted, and further polymerization reaction causes high polymerization and viscosity continues to increase so fixing strength does not decrease.

On the other hand, in the vicinity of 200-400°C when polycarbosilazane fixing strength disappears, the polycarbosilazane melted in the polymerized and solidified polysilazane acts as a plastic, offsetting the brittleness and increasing strength. At temperatures of 600°C and above, the decomposition temperature of both compounds differs so overall, there is no rapid release of gas and solidification finishes without breaking the structure. Also, as the properties of the products of reactions differ for both compounds, it is believed that by combining them, the mutual interaction contributes to increasing fixing strength.

13.

As mentioned above, through the mutual interaction brought about by the combined use of both polysilazane and polycarbosilazane compounds in the present invention, at all applied temperature ranges the prescribed high binding strength can be maintained. In the present invention, it is desirable that polysilazane and polycarbosilazane compounds employed are combined and used at an addition amount greater than 5 wt% for one relative to the other, and with a weight ratio of 1:0~0.5-40~, and preferably 1:0 ~ 1-20.

14.

In the ceramic joining compound of the present invention, a ceramic powder is added and mixed to the mixture of polysilazane compound and polycarbosilazane compound. In terms of the ceramic powder to be added, it is preferable to use a ceramics powder of the same type as the ceramics to be used or a different type of ceramics powder that matches the prescribed range of the coefficient of thermal expansion of the ceramics to be joined. When the ceramic joining compound consisted only of a polysilazane compound and a polycarbosilazane compound mixture, a good joined product could be obtained when the non-ceramics joined face was extremely small, but as the area increased the compound flaked and it was difficult to obtain a good joined product. The inventor believed that the main reason for this is that when joined ceramics are fired, the compounds convert into SiN, SiC, SiO₂ and the like, and at that time organic matter such as hydrogen and hydrocarbons separate or burn off and sublime, which causes a contraction in volume and the appearance of spaces or cracks in the joined part. By adding a ceramic powder to the polysilazane compound and polycarbosilazane compound mixture of the present invention, the contraction in volume during firing mentioned above was reduced and also the binding strength was improved.

15.

In the present invention, by utilizing ceramics powder of the same type as the ceramics to be joined, a particularly good join state can be obtained. Since thermal expansion between the joined layer and the ceramics to be joined is eliminated, it can be conjectured that thermal strain of the ceramics joined body decreases. Even if the ceramic powder is not the same as the ceramics to be joined and is a different kind, with approximately the same coefficient of thermal expansion or when the difference is less than 1×10^{-3} , a joined body with a high joining strength can be obtained.

Ceramic powders that can be added to the polysilazane compound and polycarbosilazane compound mixture that are the same kind as the ceramics to be joined are, for example, silicon powder for a silicon join, SiC powder for SiC, SiN powder for SiN, alumina powder for alumina, zirconia powder for zirconia and the like. On the other hand, for ceramic powders of a different kind which match in terms of the coefficient of thermal expansion, when the difference in the average coefficient of thermal expansion between the different ceramic powder and the ceramics to be joined is less than 1×10^{-3} , silicon, SiC, SiN, aluminum nitride and other such examples can be selected as appropriate from amongst each kind of ceramics ingredients. For example, for an aluminum nitride ceramic that will be joined, SiN or silicon powders and the like can be selected. When the difference in the average coefficient of thermal expansion between the ceramics to be joined and a different type of ceramics powder exceeds 1×10^{-3} , the ceramics joined product that can be obtained has several faults such as great thermal strain and flaking, which is not desirable.

16.

The addition amount of ceramic powder against the abovementioned compound mixture is added at a weight ratio of 1:2-40, preferably 1:4-20. When the weight ratio of ceramics powder to the total amount of the compound mixture is less than 2, there is not sufficient effect against such things as cracks when firing, and when the weight ratio exceeds 40, the joining strength decreases and it is not practical. The grain size of the ceramics powder to be added can be selected as appropriate depending on things such as the application method to be applied or the shape of the joined product. Moreover, when filling in large gaps and the like, by using large grain sized ceramics powder, contraction after drying is slight, and a favorable result can be obtained. In this case, when storing the joining compound that has been kneaded and formed, it is usually preferable to utilize ceramic powder with an average diameter of $100\mu\text{m}$ or less, as problems such as settling separation can occur with the ceramic powder.

17.

The compound of the present invention, wherein the abovementioned ceramic powder is added to the abovementioned polysilazane compound and polycarbosilazane compound mixture to obtain a powder mixture, is made into a slurry when organic solvents such as xylene are added and sufficiently kneaded. The type of solvent and the mixture ratio of solid parts and solvent can be chosen as appropriate to all the conditions when making the join. These factors are related to workability in such things as application, and generally when the amount of solvent is lower, drying is simple and volume decrease after drying is less, which means a favorable outcome can be obtained. However, when there is too little solvent, fluidity decreases and application work becomes difficult. Therefore, it is generally desirable to mix the abovementioned powder mixture of a polysilazane compound and polycarbosilazane compound mixture and ceramic powder and the solvent at a weight ratio of 1:0.05-40. To confer high fluidity, it is desirable to add solvent so that the solvent's liquid ingredients are 20 wt% and above. In the present invention, with the aim of improving workability, in addition to the abovementioned powder mixture and solvent, it is preferable to add an appropriate amount of surfactants and thickeners.

18.

The ceramic joining compound of the present invention obtained by performing the abovementioned can form a joined part by such means as applying or injecting an appropriate amount on each ceramic joining face with a brush or dispenser or the like. After applying and the like, and before the solvent evaporates and solidifies, each ceramics join part is brought together and if necessary heat is applied to dry it. After this, in an inert gas atmosphere of nitrogen, argon and the like or in an oxygen-containing gas atmosphere such as the air, by applying heating to a prescribed temperature and firing, the desired highly heat-resistant, highly strong join ceramic joined product can be obtained.

19. Embodiments

The present example is explained in more specific terms below by citing practical embodiments; however, the embodiments below do not imply any restrictions as to the present invention.

Embodiments 1-9 and Comparison Example

A compound mixture was obtained when polycarbosilazane, obtained by heating polysilane in an autoclave, was mixed at each weight ratio as shown in Table 1 against molecular weight 1700-2100 perhydropolysilazane. Silicon powder with an average grain diameter of 20 μ m was added to the mixture obtained at a weight ratio of 1:5, and a mixed powder comprising polysilazane, polycarbosilazane and silicon was obtained. Further, xylene was added so that the weight ratio would become 1:0.5 to the solid parts of the mixed powder obtained, and respective joining compounds were made after kneading for four hours in a ball mill. The joining compounds made were each approximately 30g.

20.

A silicon stick with level surfaced edges, 10mm in diameter and 30mm long, was prepared. Next, after each obtained joining compound mentioned above is applied with a silica glass bar to the edge of one silicon stick to form a joined part, it is positioned against the edge of another silicon stick and pressed together and made to adhere. The adhered silicon stick adhered component is dried at 70°C for 3 hours and the joined part is fixed. Following that, the fixed silicon stick adhered component is fired at all the respective temperatures, as shown in Table 1, in an atmosphere of nitrogen gas. Each of the fired, formed silicon joined component's tensile strengths is measured. The results are shown in Table 1.

21.

Table 1

		Weight ratio of polycarbosilazane to polysilazane	Firing temperature (°C)					
			120	300	500	800	1000	1350
			Tensile strength (MPa)					
Embodiments	1	0.05	0.2	0.5	1	2	10	40
	2	0.1	0.3	0.5	1	2.5	10	50
	3	0.5	0.5	0.6	1	2.5	10	50
	4	1	0.5	0.8	1.2	3	15	80
	5	5	0.6	1	1.2	3.5	20	100
	6	10	0.6	1	1.2	3	20	100
	7	15	0.5	0.5	1	2	15	80
	8	20	0.5	0.5	1	2	10	80
	9	40	0.5	0.3	0.5	1.5	5	30
Comparison Example	1	0	0	0.1	0.5	1.5	3	10

22.

As the above embodiments and comparison example make clear, it can be understood that when a joining compound is made from a polysilazane compound alone without the addition of polycarbosilazane, at each firing temperature, tensile strength is low, and in particular, at 120°C and 1350°C, post-firing tensile strength is very low. On the other hand, it can be seen that with a polycarbosilazane-polysilazane weight ratio of 0.2-40, and in particular, 0.1-20, the mixed joining compound has improved tensile strength after being treated at firing temperatures of 120-1350°C compared to polysilazane alone.

23.

Embodiment 10

A joining compound was made in the same way as embodiment 1, except that the weight ratio of polycarbosilazane to polysilazane was 0.3. The joining compound obtained was applied to the edge of one silicon nitride stick measuring 10mm ϕ in diameter and was pressed against another silicon nitride stick to make them adhere. This was followed by drying at room temperature and then heat treating in air at 250°C. The post-heat treated adhered silicon nitride stick was measured as in embodiment 1, and has a joining strength of tensile strength 0.5MPa. Next, the adhered silicon nitride stick mentioned above was fired in an atmosphere of nitrogen gas at 1000°C, and as a result had a joining strength of tensile strength 10MPa. Further, a joining strength of tensile strength 100MPa was obtained at a firing temperature of 1350°C.

24.

Embodiments 11-17 and Comparison Examples 2-3

A compound mixture was obtained by adding a hexamethylcyclotrisilazane polymer with an average molecular weight of approximately 1300 to polycarbosilazane used in embodiment 1, measured at a weight ratio of 1:0.2. Silicon carbide powder with an average grain size diameter of 2 μ m was added to the compound obtained, at a weight ratio shown in Table 2, to obtain a mixed powder. Further, a joining compound was made when the abovementioned mixed powder obtained was added to a mixed solvent of toluene and hexane at a ratio of 5:1, and kneaded well in a ball mill. Meanwhile, a 5 x 5 x 25 (mm) silicon carbide ceramics square bar was prepared, and using the joining compound made as outlined above, in the same way as in embodiment 1, the compound was applied to the 5 x 5 (mm) edge and two silicon carbide ceramics square bars' edges were adhered together. Next, after being dried at room temperature, the adhered bars were fired in an argon gas atmosphere at the temperatures shown in Table 2, and bending strength was measured by utilizing a four-point bending test. The results are shown in Table 2.

25.

Table 2

		Weight ratio of SiC to compound mixture	Firing temperatures (°C)					
			120	300	500	800	1000	1200
			Bending strength (MPa)					
Embodiments	11	2	0.4	0.7	1.0	1.5	3	10
	12	5	0.4	0.7	1.2	2.0	10	30
	13	10	0.5	0.8	1.5	2.5	20	80
	14	15	0.5	0.8	1.5	2.5	20	80
	15	20	0.5	1.0	2.0	2.5	20	80
	16	30	0.8	1.0	1.5	2.0	10	30
	17	40	0.5	0.5	1.0	1.0	5	10
Comparison Examples	2	0	0.3	0.5	0.2	0.3	0.5	0.5
	3	50	Not joined					

26.

As the above embodiments and comparison example make clear, compared to the joining compound of the present invention wherein bending strength increases in line with increases in firing temperatures, the joining compound of comparison example 2, in which silicon carbide ceramic powder has not been added to the compound mixture of polysilazane and polycarbosilazane, is not affected by firing temperatures and has low bending strength and no changes after firing. Moreover, it was understood that the joining compound of comparison example 3, in which silicon carbide was added at a rate over 40 times at 50 times that of the compound mixture, could not express the adherence property itself.

27.

Embodiment 18

A joining compound was obtained by mixing 5g of perhydropolysilazane, which was used in embodiment 1, 5g of polysilastylene with an average molecular weight of approximately 40000, 80g of alumina powder with an average grain diameter of 20 μ m, 45g of alumina powder with an average grain diameter of 1 μ m, and 30g of xylene and kneading them in a ball mill. Meanwhile, a 5 x 5 x 25 (mm) alumina ceramics square bar was prepared, and using the joining compound made as described above, in the same way as in embodiment 1, the compound was applied to the 5 x 5 (mm) edge and two alumina ceramics square bars' edges were adhered together. This was followed by drying and fixing at room temperature. Each of the alumina ceramics fixed bars were fired in an atmosphere of air at 500°C and 1200°C respectively, and as for embodiment 11, the bending strength was measured. The results were a bending strength of 3MPa and 60MPa, respectively.

28.

Embodiment 19

A joining compound was obtained by mixing 50g of trimethylhydropolysilazane with an average molecular weight of approximately 2000, 5g of polycarbosilazane, 200g of silicon powder with an average grain diameter of 5 μ m, 60g of diethyleneglycolbutoxyacetate, and 30g of xylene and kneading them thoroughly in a ball mill. Using the joining compound obtained, the compound was screen-printed onto a 30 x 30 (mm) square, 0.8mm thick, aluminum nitride ceramic board, and another silicon ceramic board of the same size was placed on top, pressure welded, dried and fixed. As a result of heat firing the ceramic fixed board obtained in an atmosphere of nitrogen gas at 1200°C, a joined product of strong aluminum nitride and silicon was obtained.

29. Effectiveness of Invention

The ceramic joining compound of the present invention has sufficient fixing strength with room temperature drying and not only maintains fixing strength even when being heat processed at high temperatures such as during firing but also increases joining strength so no defects of the joined part or cracking and the like occur, and with a simple process makes various types of ceramics into strong ceramic joined products, so larger and more complex shapes can be obtained.

Further, compounds comprising elements mainly such as Si, O, N, C and H in addition to ceramics powder can be utilized in the ceramic joining compound of the present invention as component ingredients. The commingling of semiconductor element contaminants can be inhibited to the greatest extent, and the compound of the present invention is of benefit as a joining material or filling material for various types of ceramic parts used in the semiconductor element manufacturing process. Moreover, the joining layer part that is formed has superior properties such as high purity, high heat resistance and high chemical resistance.

Brief Description of Drawings

Diagram 1: The diagram shows the relation between firing temperatures and joining strength in a polysilazane compound and a polycarbosilazane compound and in an equal part compound mixture of a polysilazane compound and a polycarbosilazane compound.

Diagram 1

Polysilazane
Polycarbosilazane
Mixture

Joining strength (MPa)

100
10
1
0.1

0
200
400
600
800
1000
1200
1400

Temperature (°C)